OBSERVATIONS ON THE RARE EARTHS:

I. ION EXCHANGE STUDIES ON THORIUM-RARE EARTH MIXTURES

II. X-RAY DIFFRACTION STUDIES ON CERTAIN RARE EARTH SALTS

BY

ARTHUR RALPH MATHESON

B. S., University of Illinois, 1940

M. S., University of Illinois, 1947

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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OBSERVATIONS ON THE RARE EARTHS

PART I

ION EXCHANGE STUDIES ON THORIUM-RARE EARTH MIXTURES

Introduction

The use of ion exchange materials to effect separations of the rare earths from each other is well established (1,2,3). In this investigation a cation exchange resin, Amberlite IR-100H, has been used to determine if thorium and neodymium ions could be separated from each other by this means, and a number of factors which might bear upon this separation have been studied.

The charge and hydrated radius of an ion determine its rate of exchange, and conversely, its rate of elution from the resin bed. Thorium ion would be expected to be strongly bound to the resin by virtue of its quadrivalent charge. Although the hydrated radius of the thorium ion is not known, its crystalline ionic radius is slightly less than that of neodymium. On the basis of size alone, the neodymium ion would be expected to exchange in preference to the thorium ion since larger ions are more easily exchanged. However, as shown by experimental observations, the thorium ion is the more readily exchanged ion in mixed solutions of thorium and neodymium, and thus the charge of the ion appears to be more important in this case. From the work of Boyd and his co-workers (1), it appears that the standard free energy of formation of zeolite formation, $-\Delta F_{MR}$ (298.1°K) cal./mole, increases in general with an increase in charge, irrespective of size. However, in any particular family the free energy of formation increases with an increase in ionic radius.

Since thorium is expected to be firmly bound to the resin,

it obviously would be more difficult to remove thorium ions from the resin than it would be to remove neodymium ions. However, as Tompkins and his co-workers have indicated (3), thorium is less basic than the rare earths, and the less basic materials would form more stable complexes with materials like citric acid. This property might facilitate removal of thorium with a complex-forming eluant.

Separation of Thorium and Neodymium

Solutions of thorium nitrate and neodymium chloride and mixtures of these two solutions were passed through resin beds contained in glass tubes. Both cations exchanged readily for hydrogen ion in the resin.

Materials which were investigated as possible eluting agents for the removal of the cations from the resin were five-tenths, five, and ten per cent hydrochloric acid solutions; five and ten per cent citric acid solutions; saturated ammonium oxalate solutions; saturated ammonium carbonate solutions; five per cent ammonium chloride solution; five per cent ammonium acetate solution and five per cent acetylacetone solution.

Of the above materials it was found that all except ammonium chloride, ammonium acetate, and acetylacetone solutions would elute thorium to a greater or lesser extent, and that in addition to these solutions ammonium oxalate and ammonium carbonate solutions would not elute neodymium ions from the resin. However, only certain of the eluting agents could be used for separating thorium from neodymium since materials like citric acid eluted both of the ions, and no separation was effected. By using five-tenths and five per cent hydrochloric acid solutions, in the pH range 2.60-2.88, a separation of neodymium from thorium can be effected. By using saturated ammonium carbonate solutions, pH 8.56, and saturated ammonium oxalate solutions, pH 5.15, 6.28, and 8.70, a separation of thorium from neodymium can be effected. To elute both ions separately,

it was necessary after one species of ions had been eluted to change to another eluting agent which would elute those ions remaining in the column.

In no case were all of the thorium ions eluted from the resin, and it was necessary to ash the resin to recover the remainder of the thorium. It is believed that the thorium may be bound in the interior of the resin particle or molecule by a coordinate linkage and thus not be removed readily, even by a strong complexing agent such as ammonium oxalate.

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PART II

X-RAY DIFFRACTION STUDIES ON CERTAIN RARE EARTH SALTS

INTRODUCTION

The crystal structures of the rare earth elements and many of their compounds have been characterized by means of x-rays.

In this study, a brief discussion of the crystal structures of the rare earth elements, oxides, and halides has been given, and a list has been compiled of those rare earth elements and compounds whose crystal structures have been

determined together with pertinent references. In addition, as much experimental data as possible concerning the crystal structures of certain available rare earth compounds have been obtained.

Experimental and Results

Powder patterns were prepared for neodymium bromate ennea-hydrate, neodymium sulfate octa-hydrate, and praseodymium, neodymium, and thorium acetylacetonates. The interplanar distances for these compounds were calculated, and it appears that praseodymium and neodymium acetylacetonates are isomorphous. It was not possible to determine if thorium acetylacetonate was isomorphous with the other compounds.

Large single crystals of neodymium acetylacetonate were available and were used in the determination of the crystal structure of this compound.

From optical examination, rotation patterns, and Weissenberg patterns of the single crystals, it appears that neodymium acetylacetonate has a monoclinic structure, with a probable space group $C_{2h}^5 - P2_1/c$, with 4 molecules per unit cell. The lattice constants were determined to be $a = 11.56 \pm 0.05$ A., $b = 11.25 \pm 0.07$ A., and $c = 15.81 \pm 0.07$ A., $\beta = 110° 24'$, density $= 1.526$ g./cm.^{3}. From these data and from the work of Astbury (1), it appears that neodymium and gallium acetylacetonate have isomorphous crystal structures.

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VITA

The author was born on October 7, 1915, in Kansas City, Missouri. He attended the public schools of that city and of Clay County, Missouri, until his graduation from North Kansas City High School in May, 1933.

In September, 1936, he entered the University of Illinois and received the degree of Bachelor of Science in chemistry in June, 1940.

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In March, 1946, the author entered the Graduate School of the University of Illinois. He received the degree of Master of Science in chemistry in February, 1947. He held a teaching assistantship in Inorganic from February, 1946, to February, 1947. From February, 1947, to June, 1948, he held a half-time research assistantship sponsored by the Office of Naval Research.

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He is a joint author of the following papers:

1. Nicholson, D. G., and Matheson, A. R., Paint, Oil and Chem. Rev., **102,** No. 7, 44 (1940).
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